

Development of Detailed and Reduced Kinetic Mechanisms for Surrogates of Petroleum-Derived and Synthetic Jet Fuels:

Drexel Flow Reactor Studies at Low and Intermediate Temperatures

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Program Overview

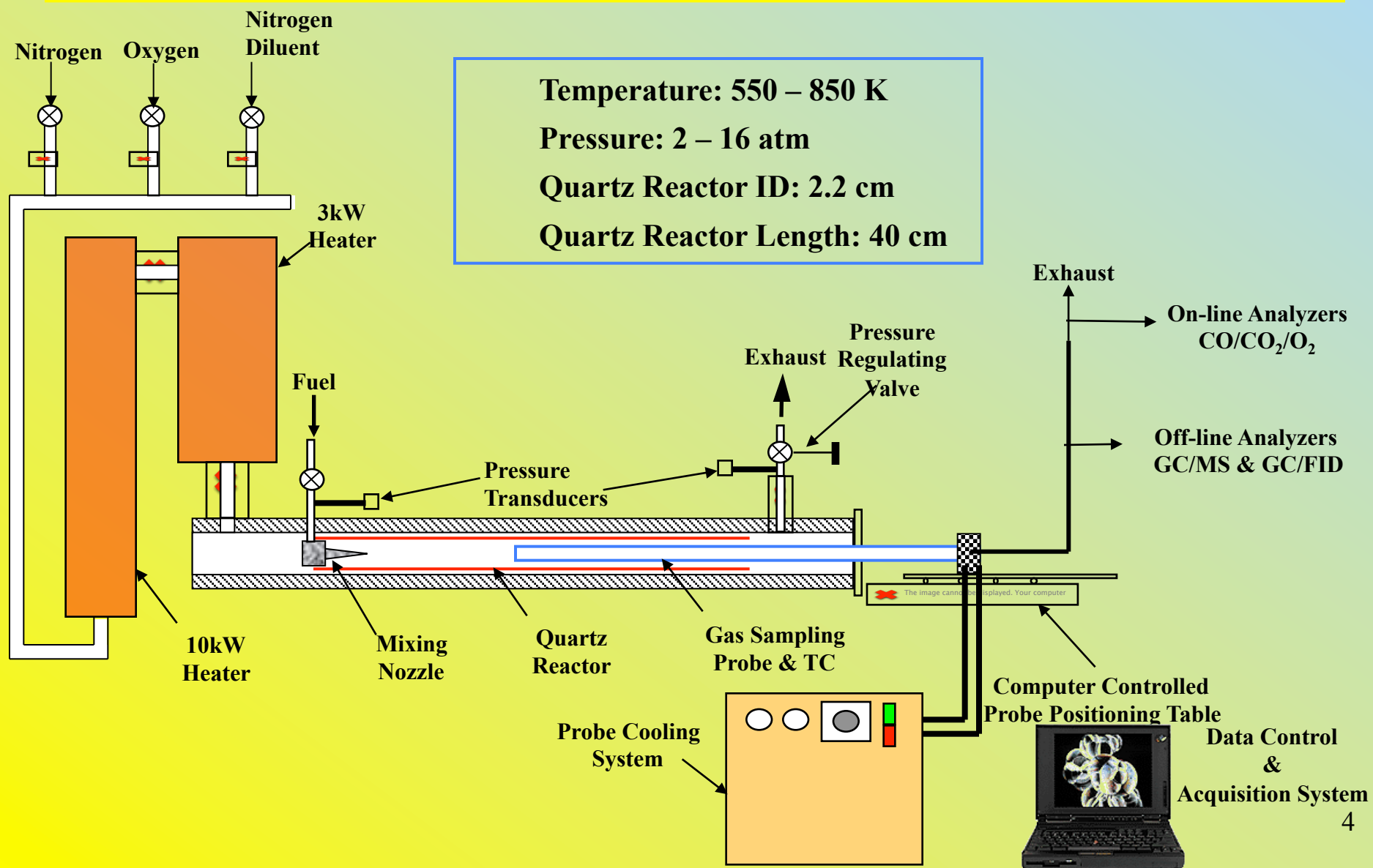


- **Objectives:**
 - 1) Explore the preignition oxidation behavior of petroleum and alternative jet fuel surrogate components
 - 2) Quantify the combustion properties of the surrogate components
 - 3) In Year 2, n-dodecane and n-butylcyclohexane studies
- **Approach:**
 - React the fuel/oxidizer/diluent systems under well-controlled conditions in our Pressurized Flow Reactor (PFR)
 - » Perform bench scale tests on n-dodecane and n-butylcyclohexane
 - Coordinate with Stanford flow reactor experiments at higher temperatures
 - » Monitor reactivity and collect gas samples as a function of experimental and reactant conditions
 - » Perform detailed chemical analysis of extracted gas samples
 - Mechanistic analysis and development
 - Provide data for chemical kinetic model development

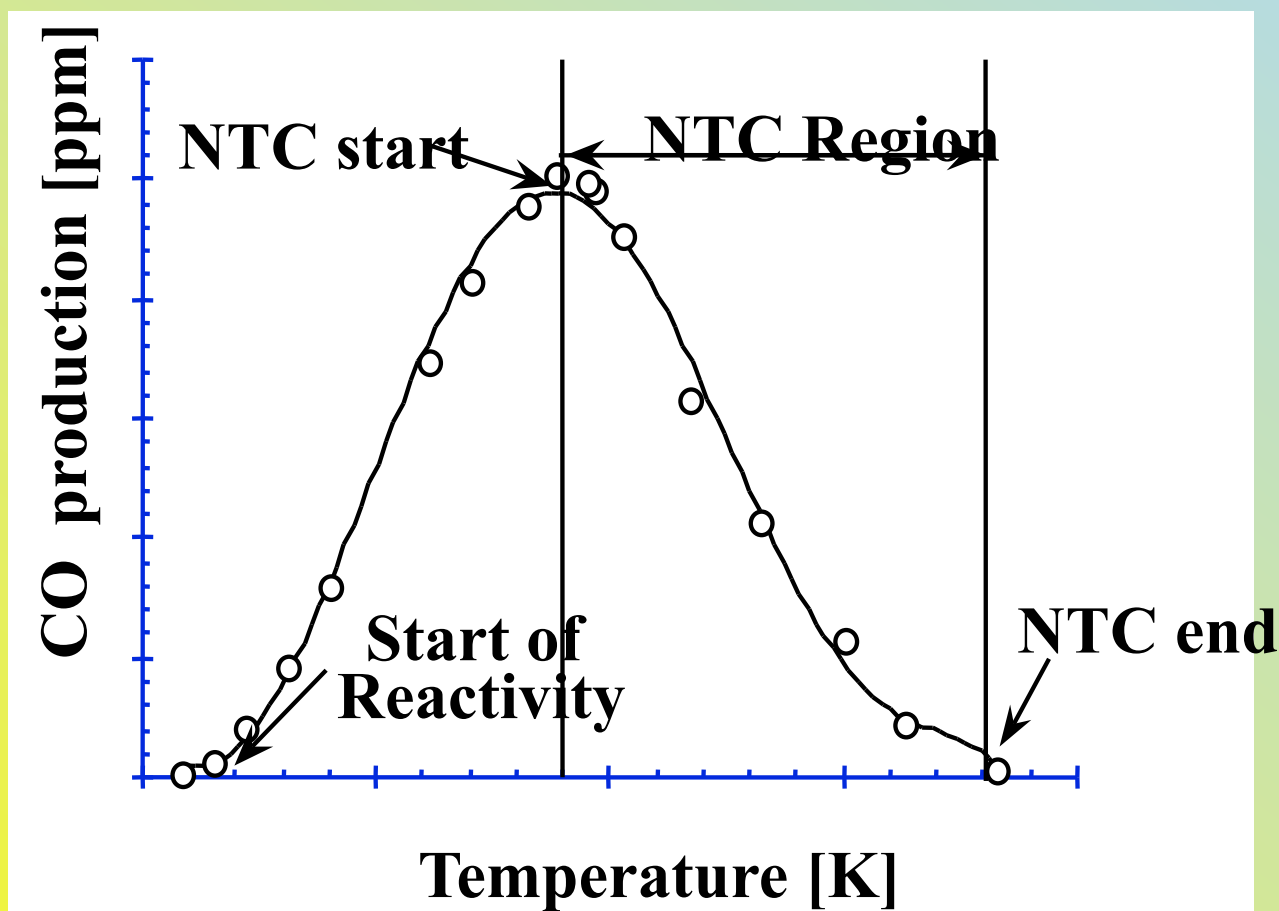
Motivation

- **Detailed kinetic models will aid in the development and optimization of the next series of advanced air-breathing propulsion systems and their use with alternative fuels**
 - **Model development and verification require quantitative characterization of combustion properties**
- **Oxidation at low and intermediate temperatures (500-1100 K) in model validation and particularly important in CI engines**
 - **High-quality, reproducible data quantifying the combustion of possible JP-8 surrogate components at these conditions is scarce**

PFR Facility



Representative Reactivity Map Profile

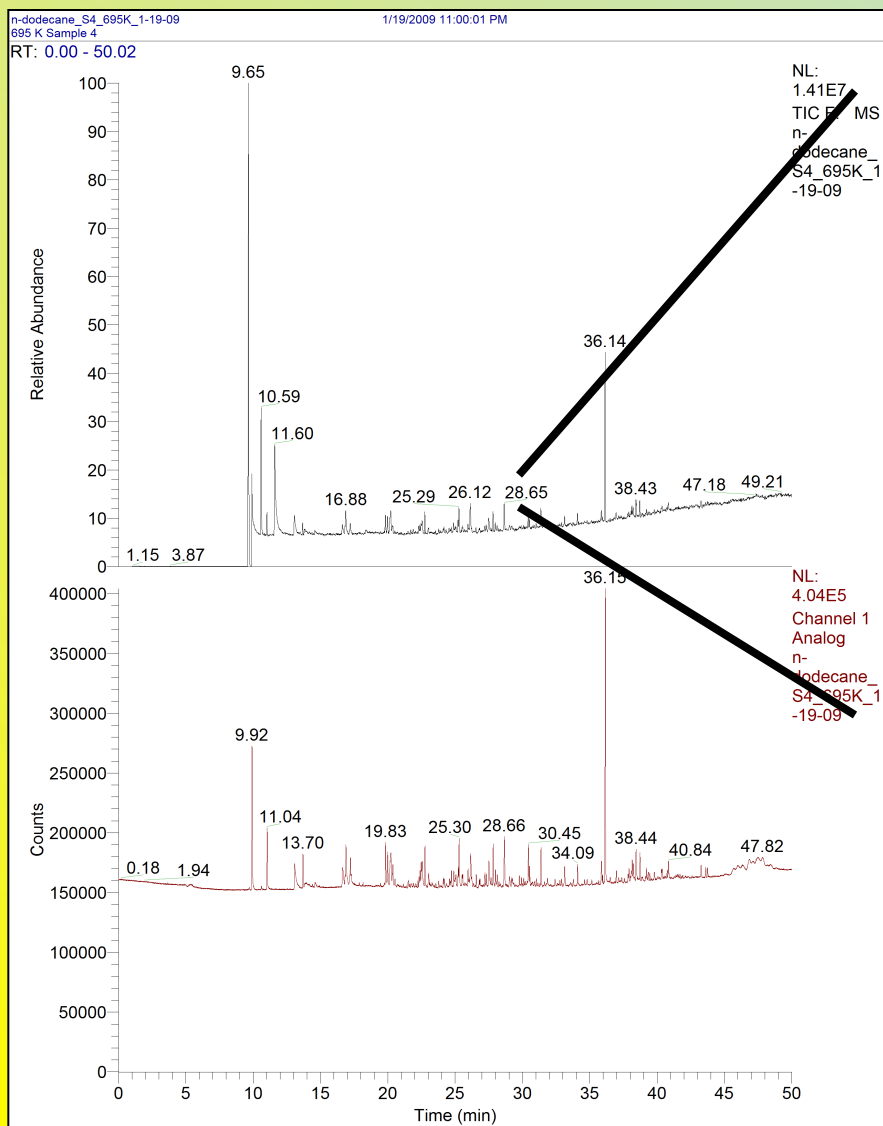


- CO is a major indicator of reactivity at low temperatures, we also measure water with the MS which tracks the CO
- Negative Temperature Coefficient (NTC) region is the shift from low to intermediate temperature chemistry

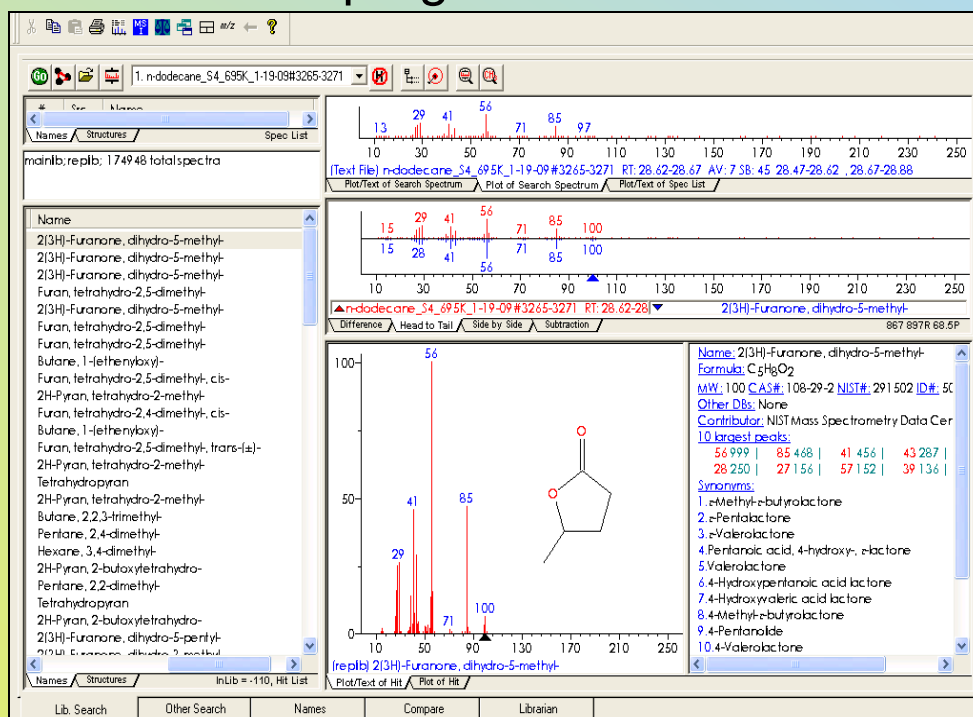
GC/MS/FID Facility

- **Samples injected at 570 Torr into GC/MS/FID for analysis**
- **Separation aided by sub-ambient initial oven temperature and then ramped up to 250°C**
- **Supelco Petrocol DH column in GC**
 - **100 m, 0.5 μm film thickness**
 - **0.25 mm OD, 1250 Phase Ratio (β)**
- **MS parameters**
 - **Ion source 200°C**
 - **Electron ionization -70 eV**
 - **Multiplier voltage 1456 V**
 - **Emission current 100 μA**

GC/MS/FID Analysis



MS database program



- Species are identified from GC/MS chromatograms and comparison to mass spectra from the NIST MS 2.0 database of 150,000 compounds

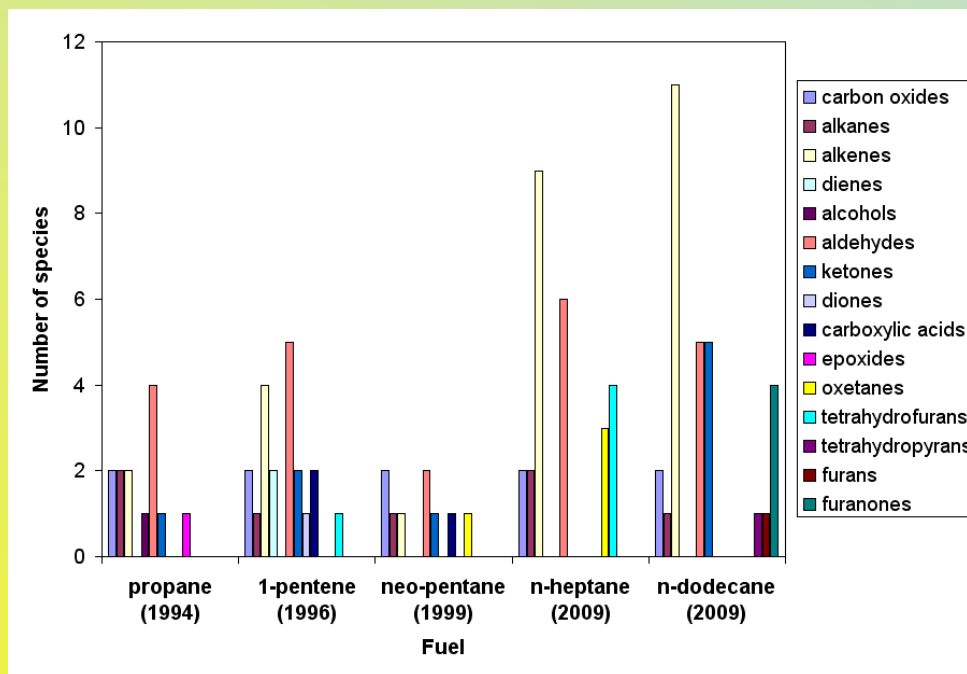
Other Measurements

- **Measure CO/CO₂/O₂ with on-line analysis**
 - Errors are ± 50 ppm for CO and CO₂ from NDIR analyzer, and ± 1250 ppm for O₂ from electrochemical oxygen cell
- **Measure F/O₂ ratios with GC/MS/FID combined with O₂ Analyzer to calibrate equivalence ratio before each experiment**
- **FID Calibration of lighter hydrocarbons ($n < 7$) uses purchased gas-phase standards at 15, 100, and 1000 ppm**
- **Calibration of heavier species is achieved with correction factors of FID signals that account for differences in carbon, hydrogen, and oxygen numbers between different molecules of similar structures (Schofield, 2008)**

Review of Year 1 Work

- A series of n-dodecane experiments was conducted at low temperatures (550-850 K) at a range of equivalence ratios (0.2-0.9)
 - Carbon balances were not acceptable - on average 50%, and as low as 20%, depending on the temperature
 - Obviously, the intermediates from the oxidation of n-dodecane posed new analytical problems

Past PFR Work



Year 2 Work – Experimental Upgrades

- **Identify sources of poor carbon balances**
 - **Sample/Hold System (heated storage loops) was shown to “degrade” sample over the 18 hours of storage between collection and analysis of final loop**
 - **Transfer lines between PFR – cart – GC were found to produce problems through a variety of mechanisms: cold spots at valves and fittings (condensation), poor flow patterns (dead volumes), heated stainless steel lines (reaction)**
- **System redesign - samples are transferred directly to the GC/MS/FID with heated, glass-lined stainless steel transfer lines**
- **Operational adjustment - PFR is maintained at operating temperature while each sample is analyzed by GC/MS/FID**
- **Carbon balances are now greater than 80% for n-dodecane**
 - **Number of species measured for n-dodecane increased from 30 to 115**

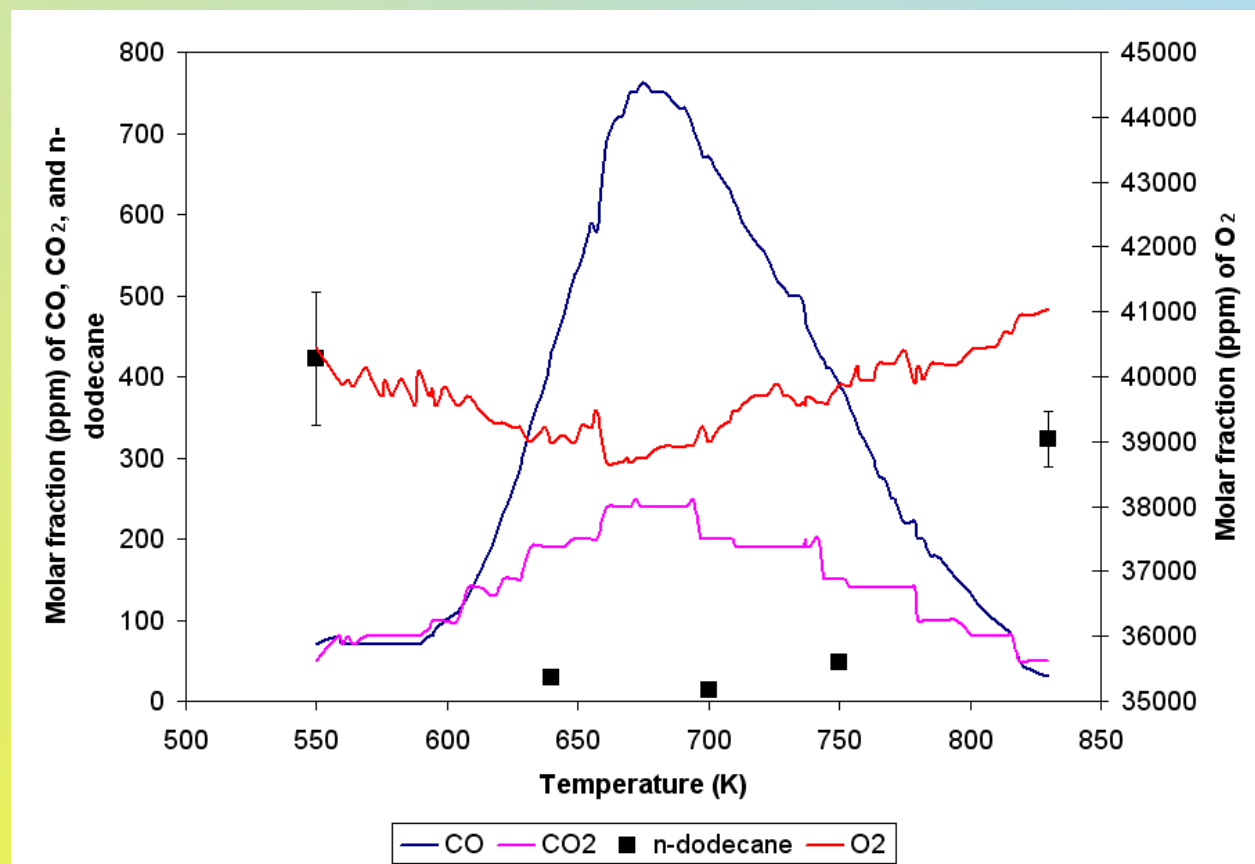
Experimental Conditions

	n-Dodecane	Uncertainty	n-Butylcyclohexane	Uncertainty
Fuel (ppm)	531	± 8	1082	± 19
O₂ (ppm)	42,100	± 1250	42,100	± 1250
ϕ	0.23	± 0.05	0.38	± 0.05
N₂	balance	-	balance	-
Pressure (atm)	8.00	± 0.025	8.00	± 0.025
Residence time (ms)	120	± 10	120	± 10

- Fuel concentrations, and intermediate species in the following graphs, are the average of three experiments for each fuel
- Fuel uncertainties, and intermediate species error bars in following graphs, are ± 1 standard deviation of the three experiments
- O₂, equivalence ratio, pressure, and residence time uncertainties are based on instrumental uncertainty

Reactivity Mapping of n-Dodecane

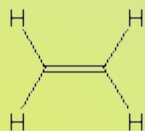
- **550 K < T < 700 K:**
increasing reactivity
- **T ~ 700 K:** NTC start
- **700 K < T < 850 K:**
NTC region
- **Minimum carbon balance 80%; 115 peaks measured**



- In the low temperature regime, CO₂ is produced from oxygenates such as cyclic ethers (Glaude et al., 2002)
- H₂O was measured using the MS and matched the CO trend

Glaude et al. (2002), *Energy Fuels* 16:1186-1195.

Key Alkenes from n-Dodecane



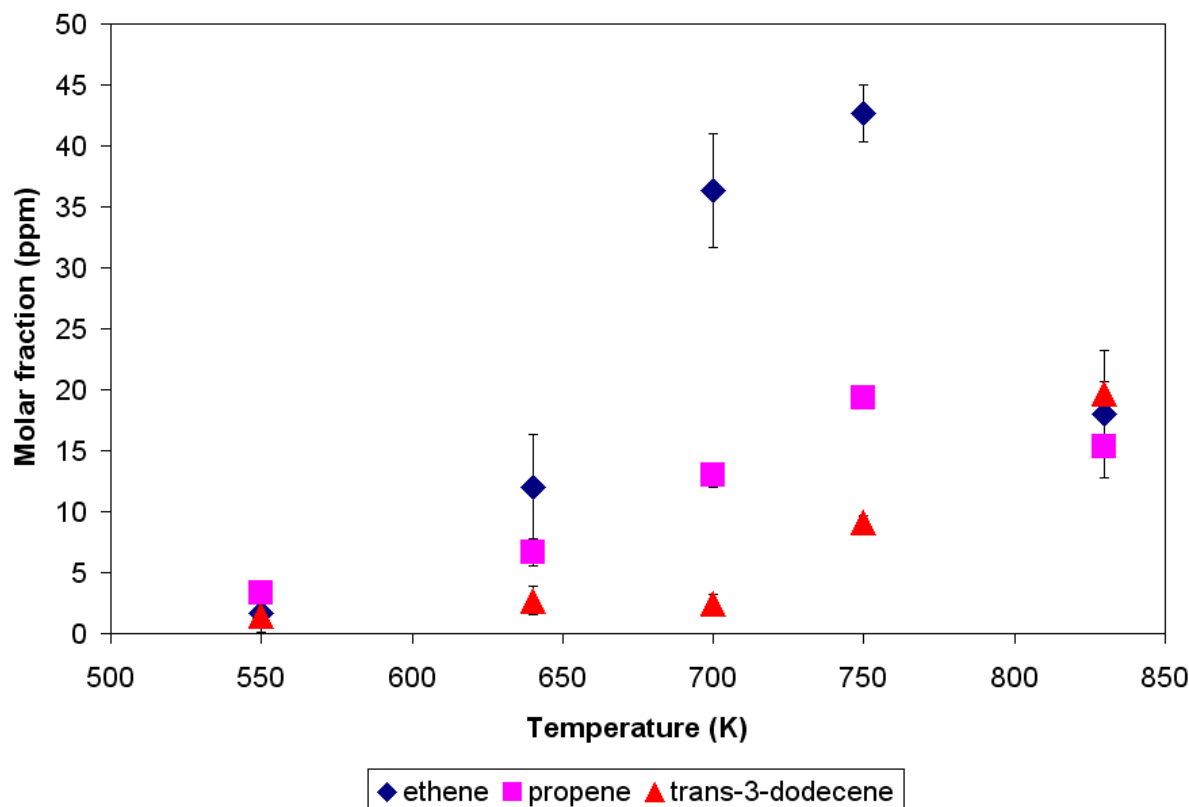
ethene



propene

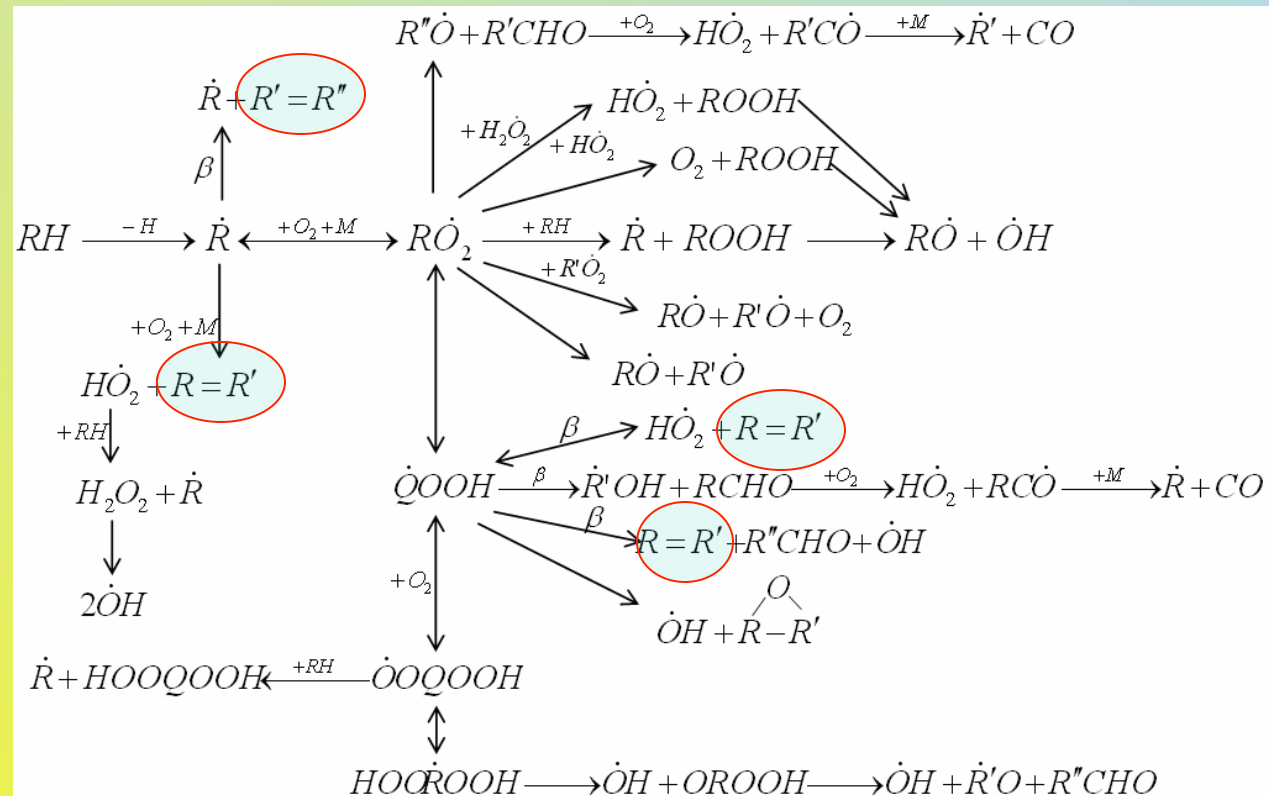


trans-3-dodecene



- Other alkenes, dienes, and alkynes produced at smaller quantities
- In NTC region, H-abstraction of alkyl radical by O_2 produces conjugate alkene (Ciajolo and D'Anna, 1998)

Alkane Oxidation Mechanism – Alkene Formation



- **Low temperature reactivity:** low levels of alkenes produced from β -scission of alkylhydroperoxy ($\text{QOOH}\cdot$) radicals
- **NTC:** high levels of alkenes produced from β -scission of alkyl ($\text{R}\cdot$) radicals and H-abstraction by O_2 of $\text{R}\cdot$

Key Aldehydes from n-Dodecane

acetaldehyde



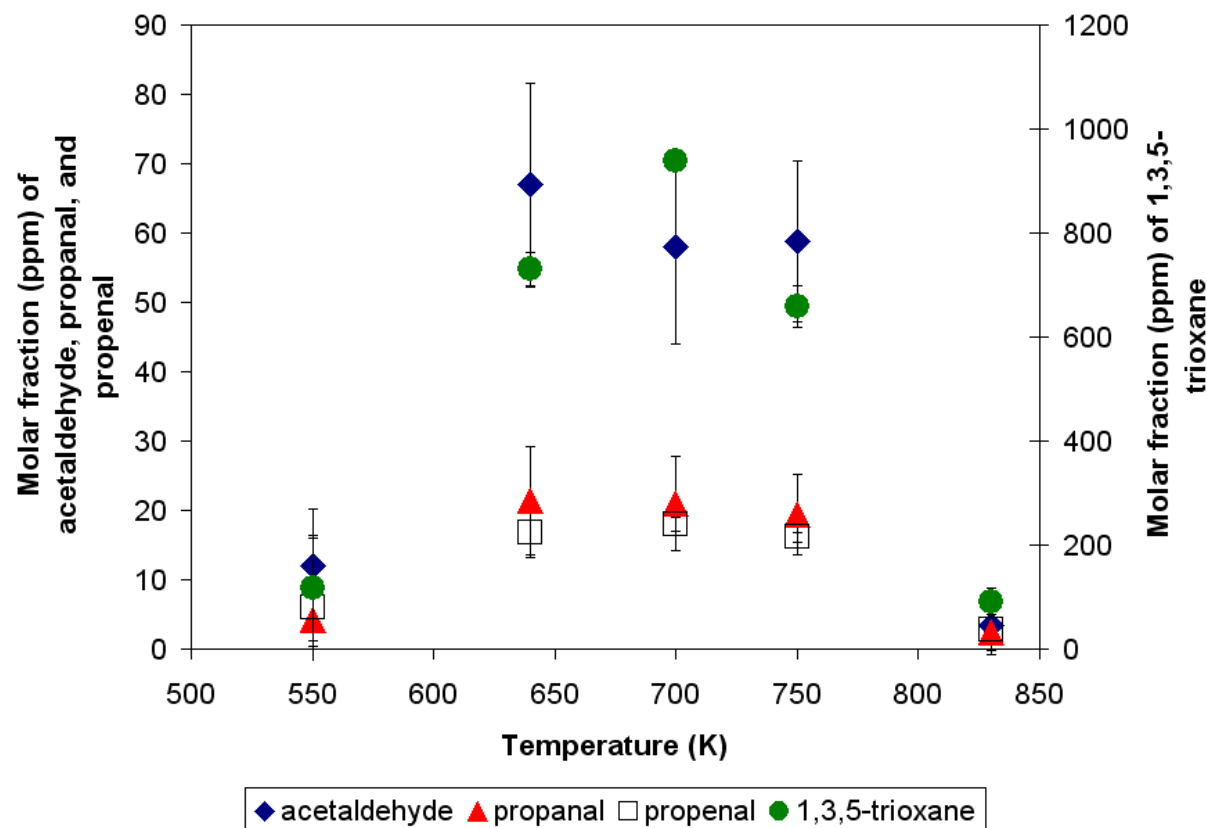
propanal



propenal

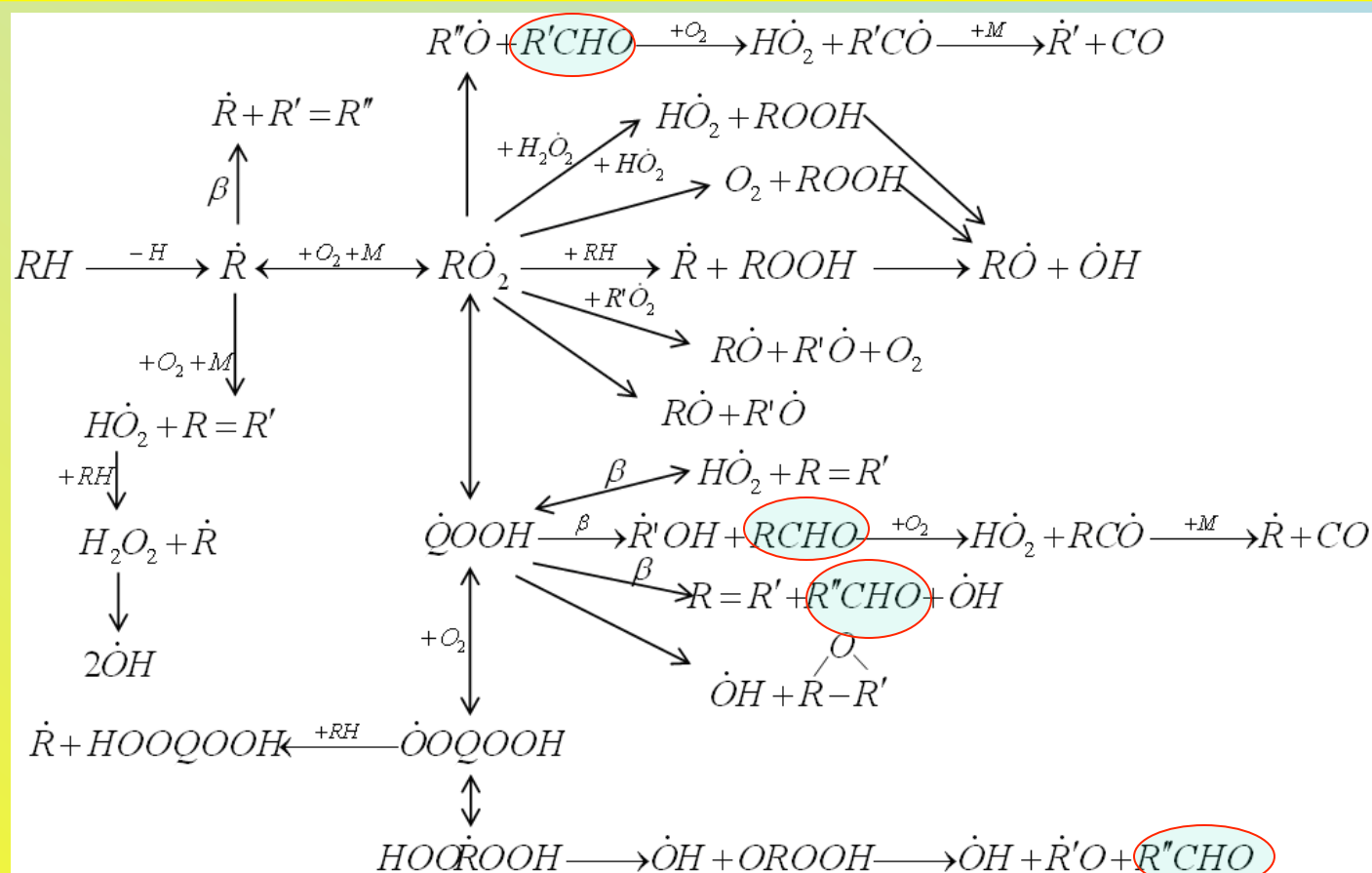


1,3,5-trioxane



- Aldehydes peaked near start of NTC
- 1,3,5-trioxane probably from formaldehyde
 - Up to 40% of carbon is measured as 1,3,5-trioxane at NTC start
- Other aldehydes produced at smaller quantities

Alkane Oxidation Mechanism – Aldehyde Paths

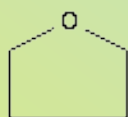


- **Low temperature reactivity:** low levels of aldehydes produced from β -scission of alkylhydroperoxy (QOOH·) radicals and destruction of alkylperoxy (RO₂·) radicals
- **NTC start:** high levels of aldehydes produced from ketohydroperoxides (OROOH)

Cyclic Oxygenates from n-Dodecane



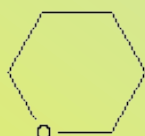
dihydro-2(3H)-furanone
(γ -butyrolactone)



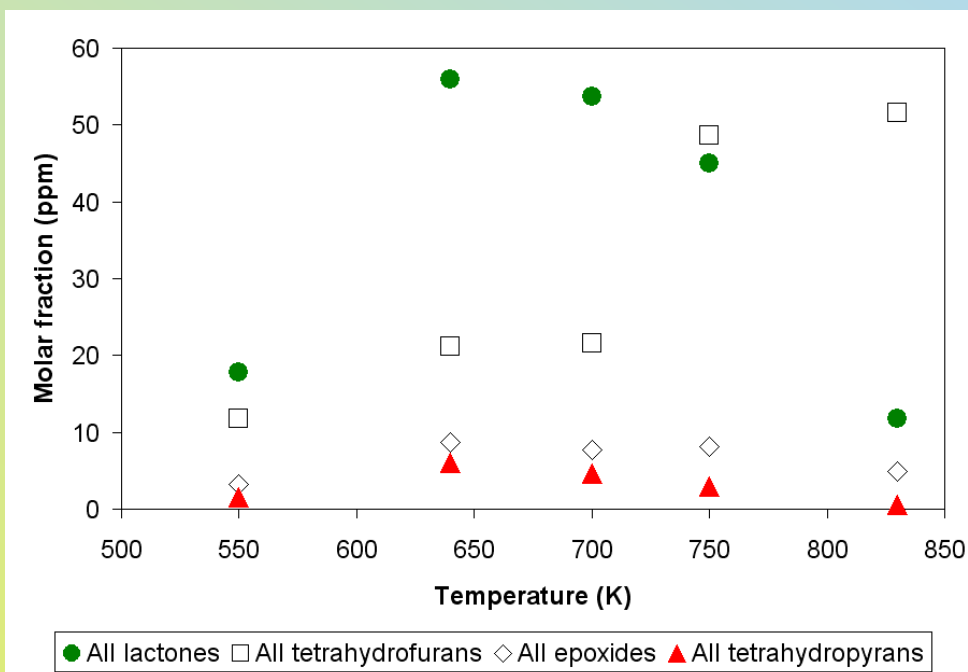
tetrahydrofuran



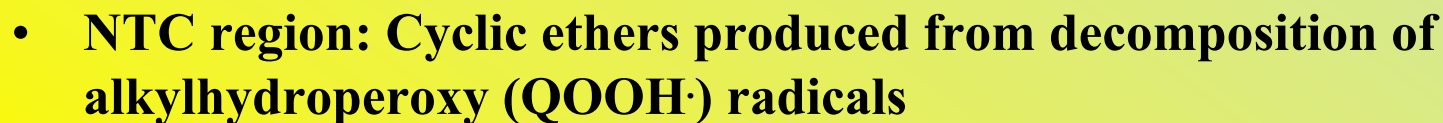
ethylene oxide



tetrahydropyran

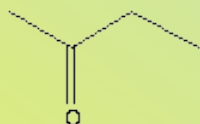


- Alkylated lactones and cyclic ethers (mainly 5-membered rings) were measured
 - Pathway to 5-membered rings provides chain branching, while 3-, 4-, or 6-membered rings provide chain propagation (Westbrook et al., 2009)
- Tetrahydrofurans increased in NTC region
- Dagaut et al. (1994) measured cyclic ethers from n-decane oxidation at 550-1150 K and 0.1-1.5 ϕ , but did not observe lactones

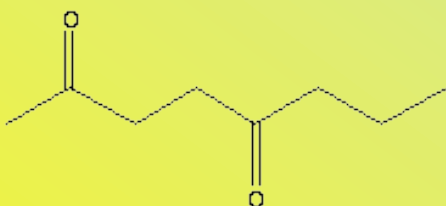
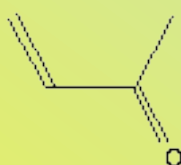


Ketones from n-Dodecane

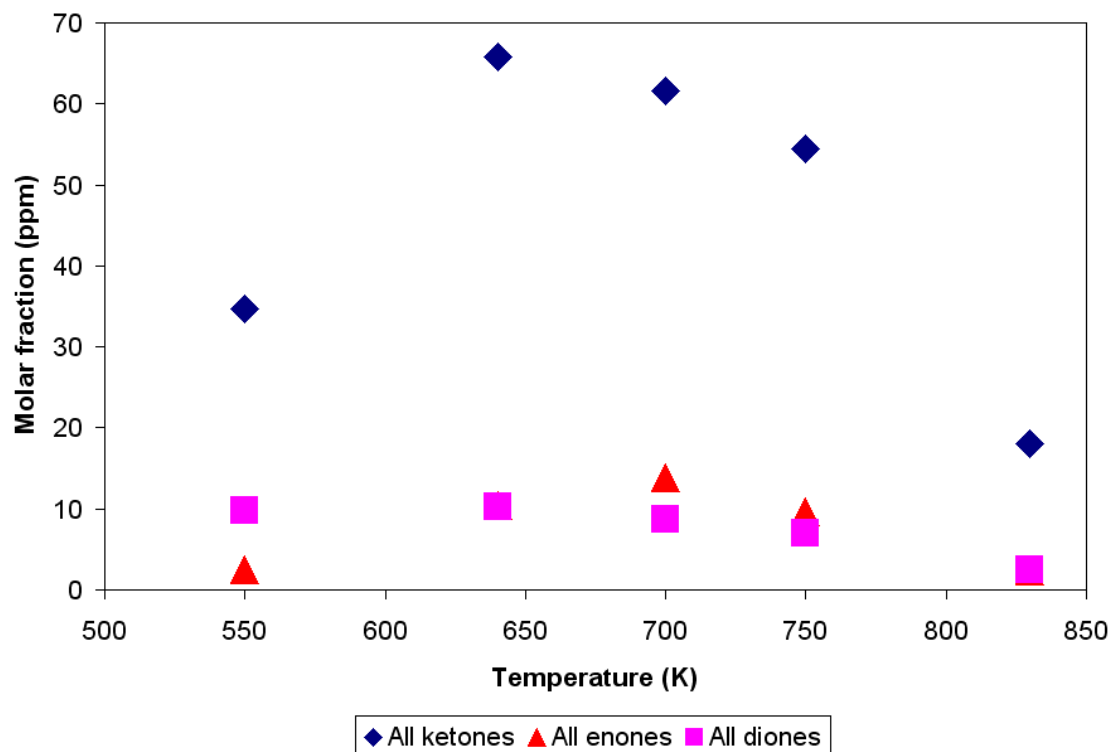
butanone



methyl vinyl
ketone



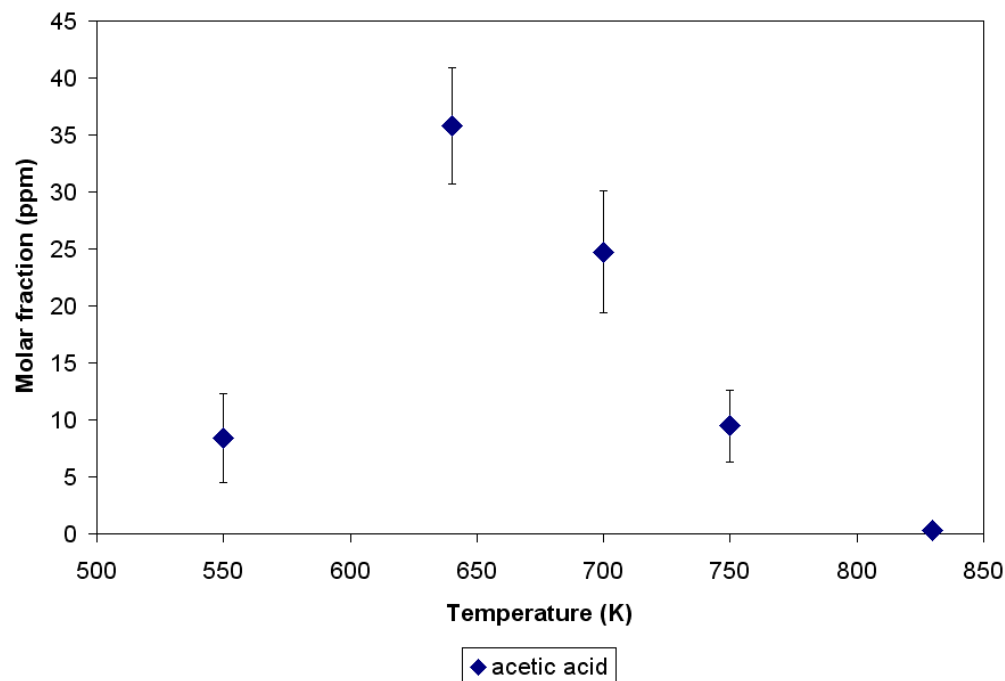
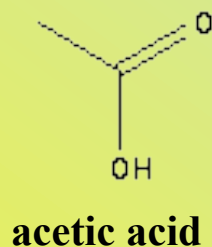
2,5-octanedione



- Ketones, diones, and enones (unsaturated ketones) peaked at NTC start
- Alkylhydroperoxy radicals ($\text{QOOH}\cdot$) can decompose to ketones (Glaude et al., 2000)

Glaude et al. (2000), *Comb Flame* 122:451-462.

Key Carboxylic Acid from n-Dodecane

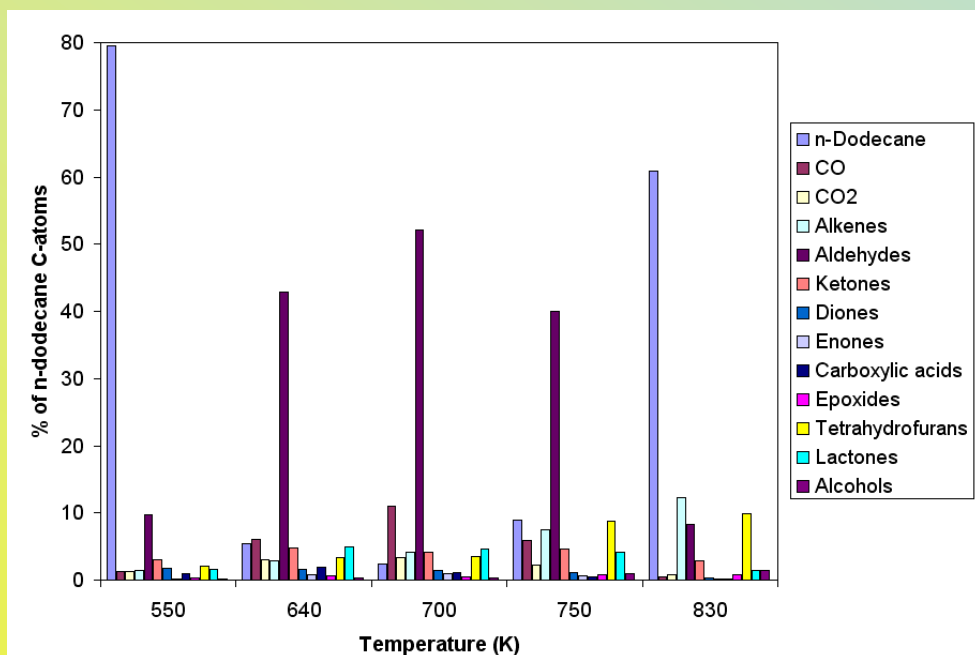


- Acetic acid peaked prior to NTC start
- Decomposition of ester can yield acid and alkene (Schwartz et al., 2006; Metcalfe et al., 2007)
 - Esters not observed in present work, but cyclic esters (lactones) observed

Schwartz et al. (2006), *J Phys Chem A* 110:6643-6648.

Metcalfe et al. (2007), *J Phys Chem A* 111:4001-4014.

Class Analysis – n-Dodecane



All classes accounting for $\geq 1\%$ of reactant, fractions of reactant and product calculated by C-atoms

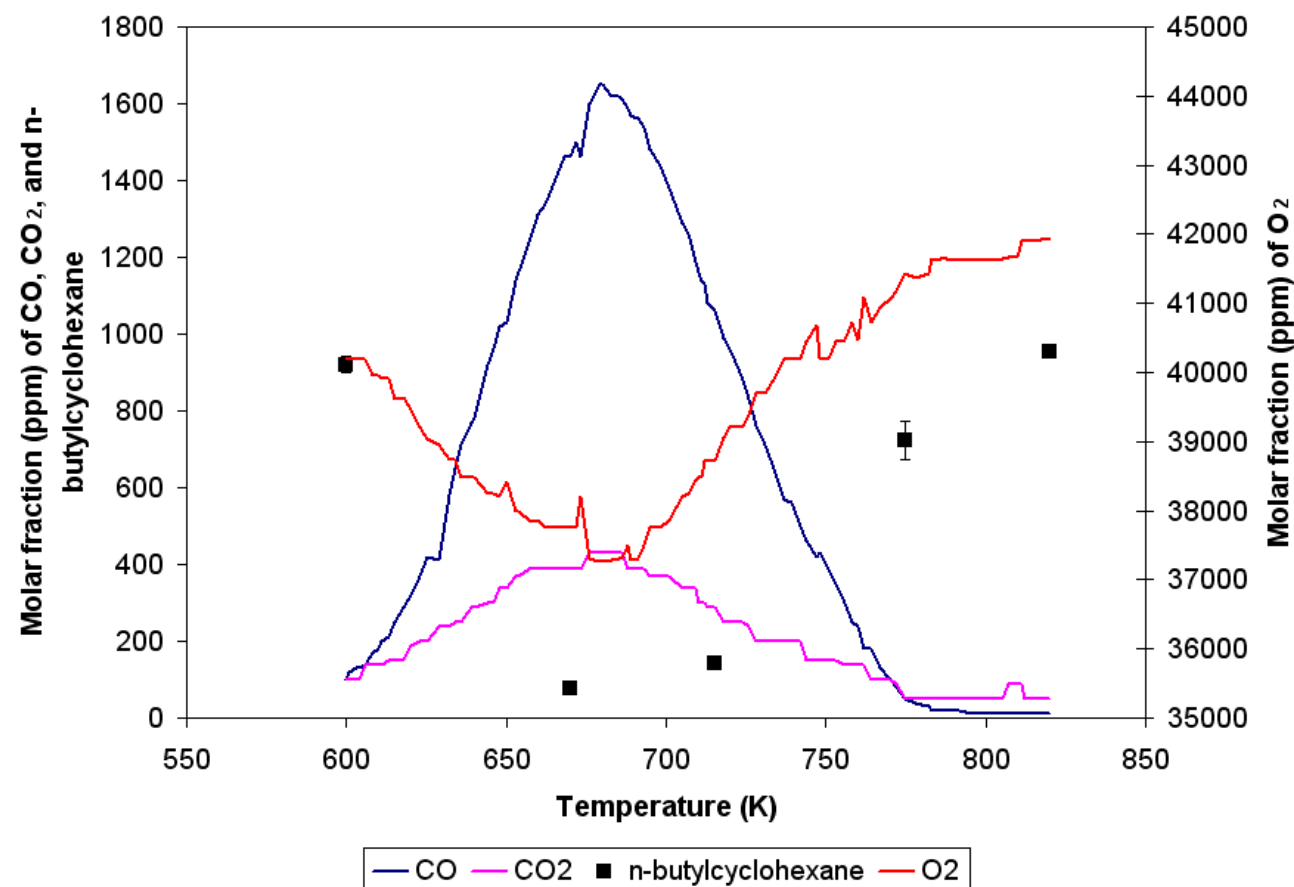
Temperature (K)	550	640	700	750	830
Classes accounting for $\geq 5\%$ of reactant, listed in descending order	dodecane, aldehydes	aldehydes, CO, dodecane, lactones, ketones	aldehydes, CO, lactones	aldehydes, dodecane, THF's, alkenes, CO, ketones	dodecane, alkenes, THF's, aldehydes

Highlights of n-Dodecane Work

- **Modifications to the PFR improved carbon balance which will help for reaction pathway analysis and model development**
- **CO, CO₂, and aldehydes all peaked at start of NTC**
- **Different hydrocarbon classes were predominant at different reaction conditions:**
 - **Low temperature (lactones and ketones)**
 - **NTC start (lactones)**
 - **Over NTC region (alkenes, tetrahydrofurans, and ketones)**
- **Novel observations, compared to past work of lighter hydrocarbons at these temperatures, included the identification of many species with two O atoms - lactones, carboxylic acids, and diones**

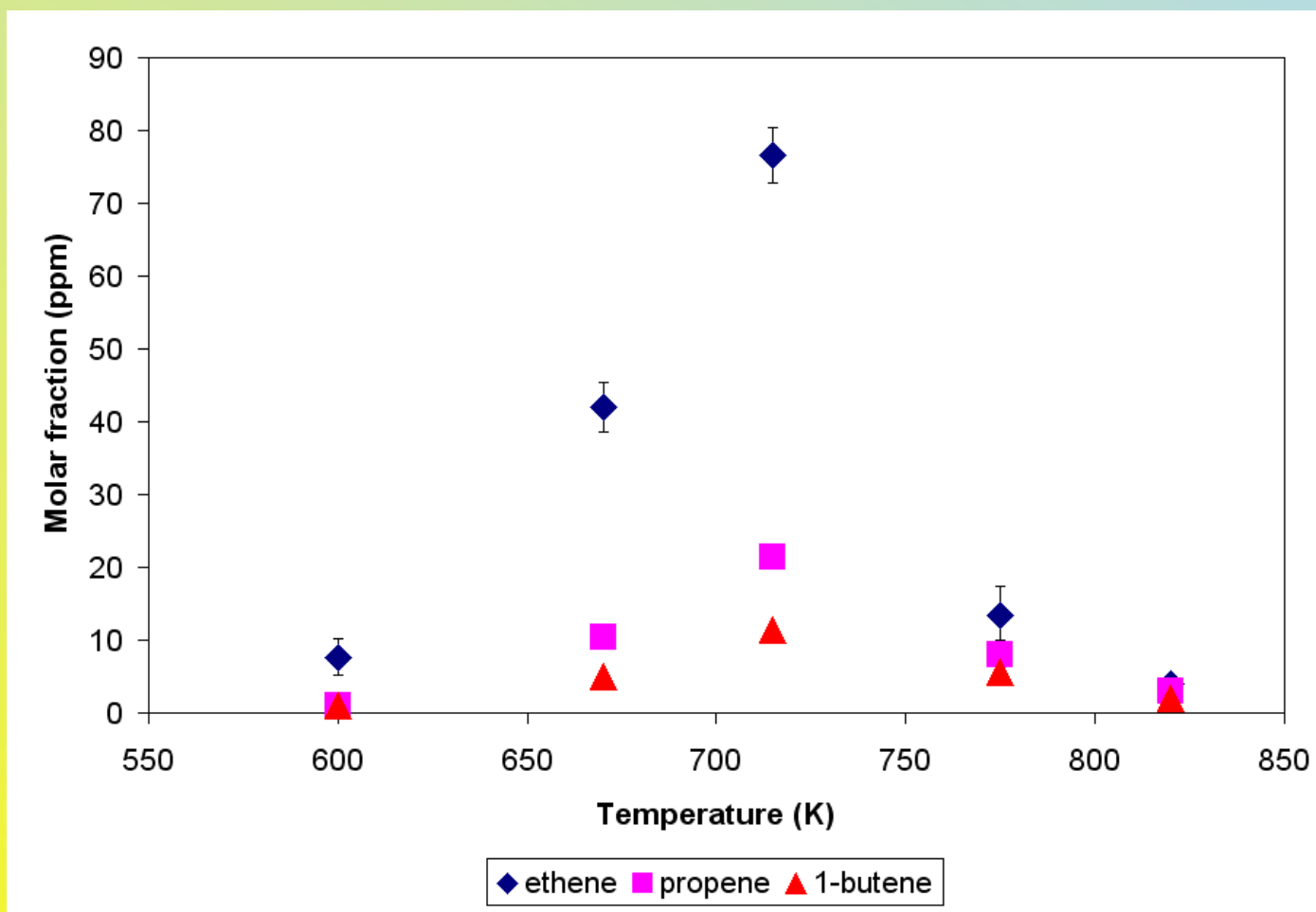
Reactivity Mapping of n-Butylcyclohexane - nBCH

- **600 K < T < 700 K:**
increasing reactivity
- **T ~ 700 K:** NTC start
- **700 K < T < 850 K:**
NTC region
- **Minimum carbon balance 95%; 65 peaks measured**



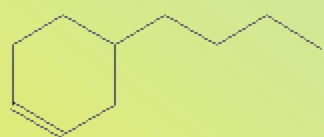
- H₂O was measured using the MS and matched the CO trend

Key Straight-chain Alkenes from n-BCH

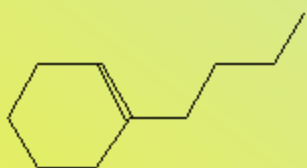


- Straight chain alkenes were C_{2-4} and thus likely produced from n-butyl chain

Key Cycloalkenes from n-BCH



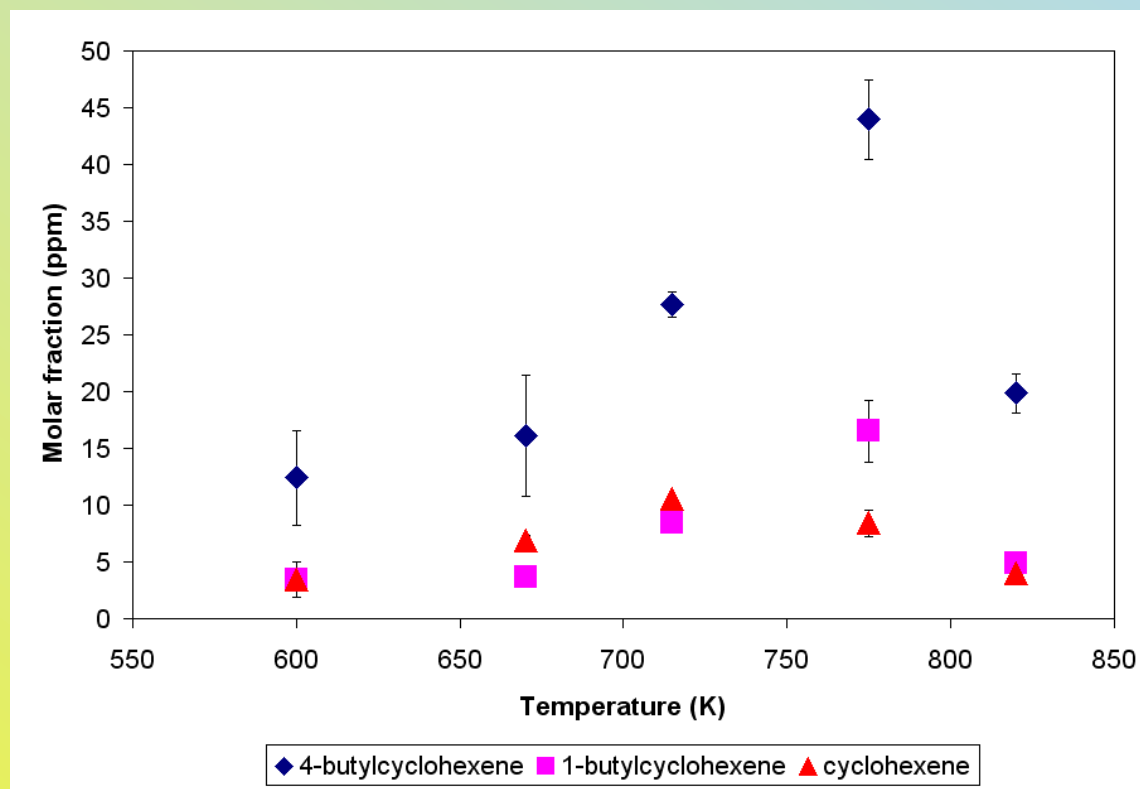
4-butylcyclohexene



1-butylcyclohexene

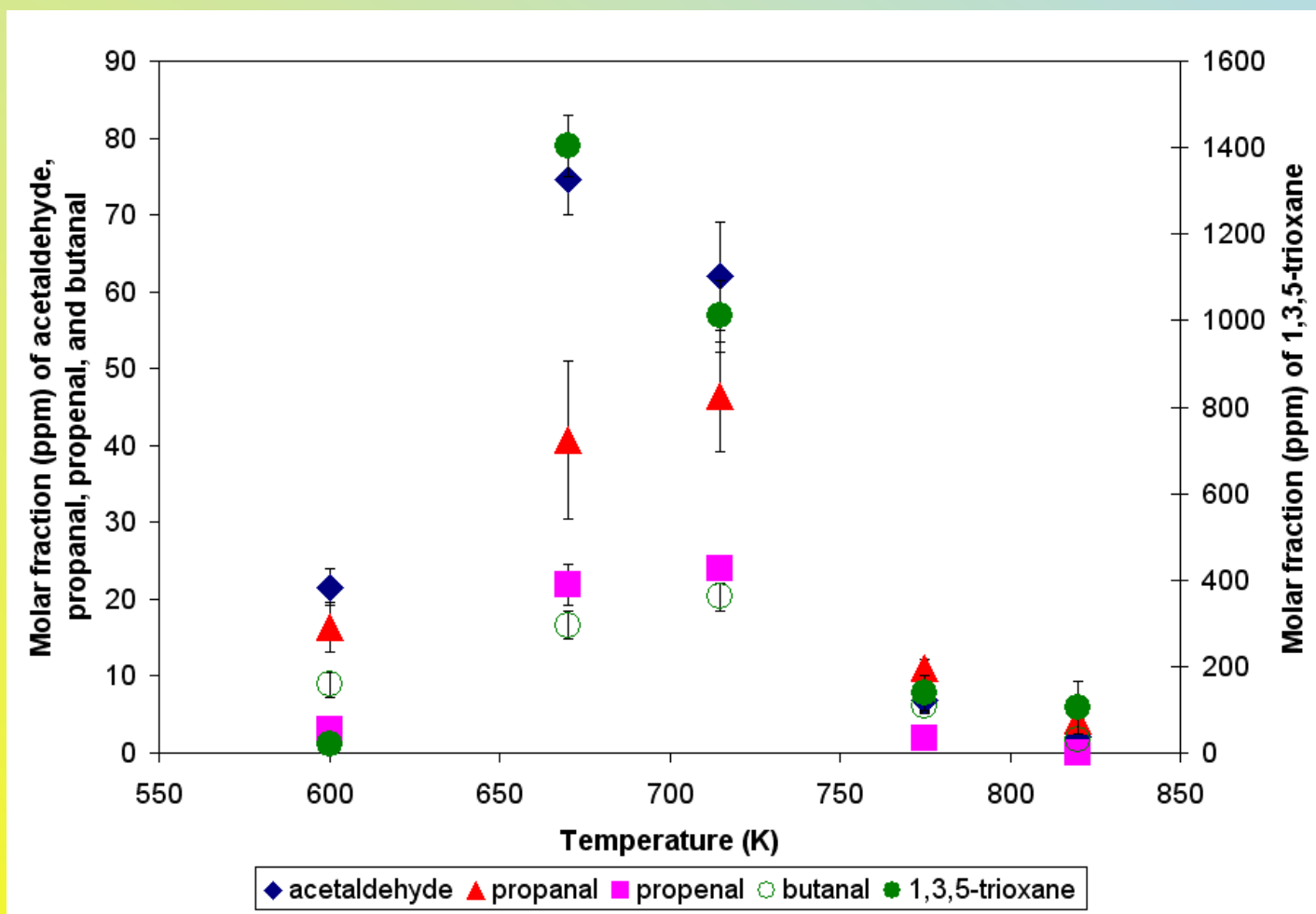


cyclohexene



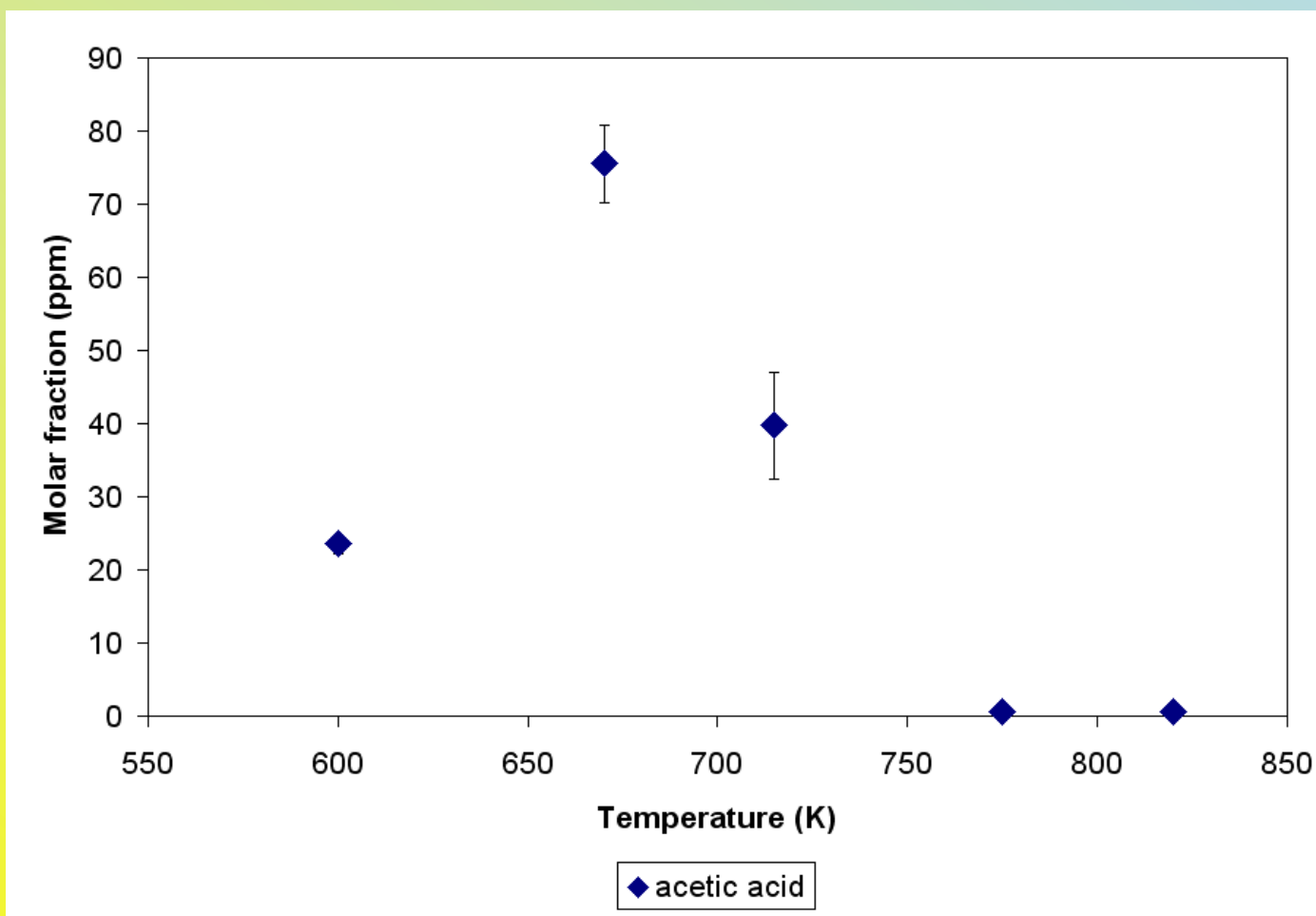
- Butylcyclohexenes highest in NTC region where overall reactivity is low
- In high temperature methylcyclohexane oxidation, β -scission of cyclohexyl radical yielded cyclohexene (Zeppieri et al., 1997)

Key Aldehydes from n-BCH



- Aldehydes highest around NTC start
- 1,3,5-Trioxane polymerized from formaldehyde during sampling

Key Carboxylic Acid from n-BCH



- Acetic acid peaked around NTC start

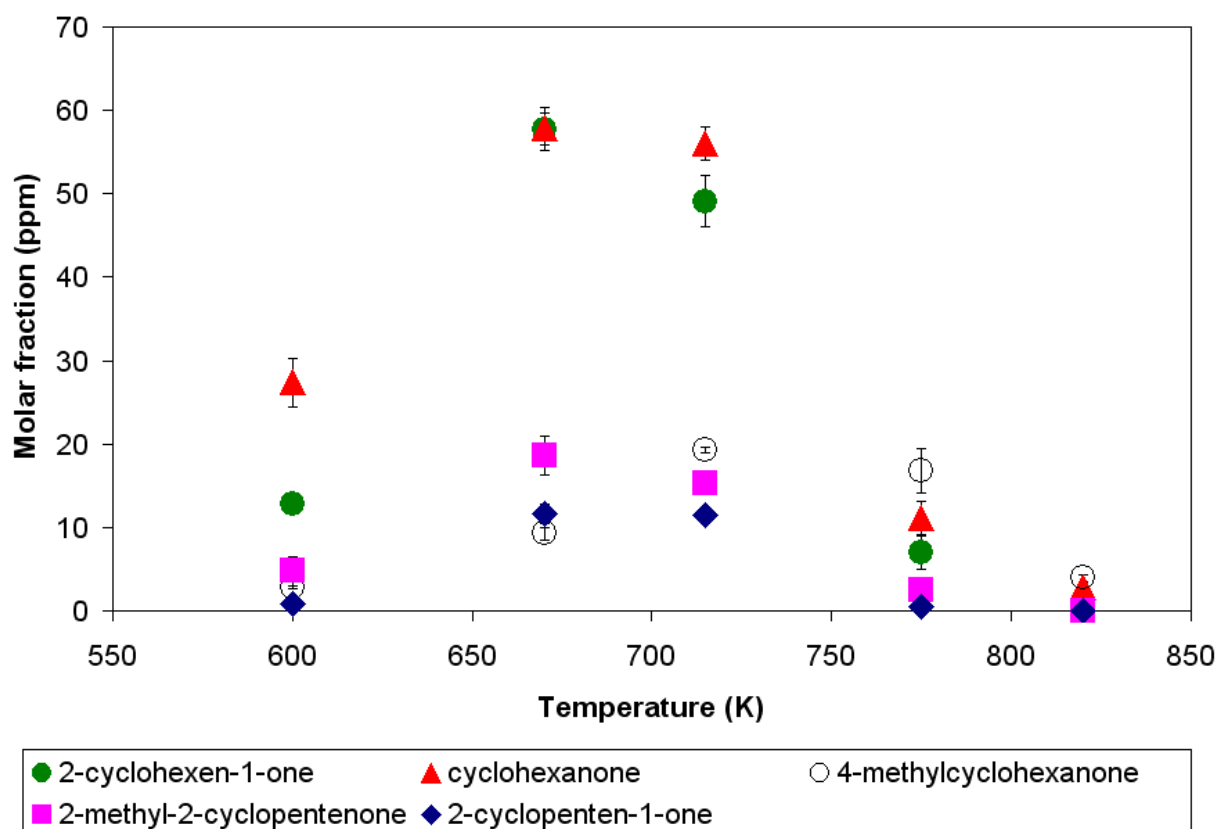
Key Cycloketones from n-BCH



cyclohexanone



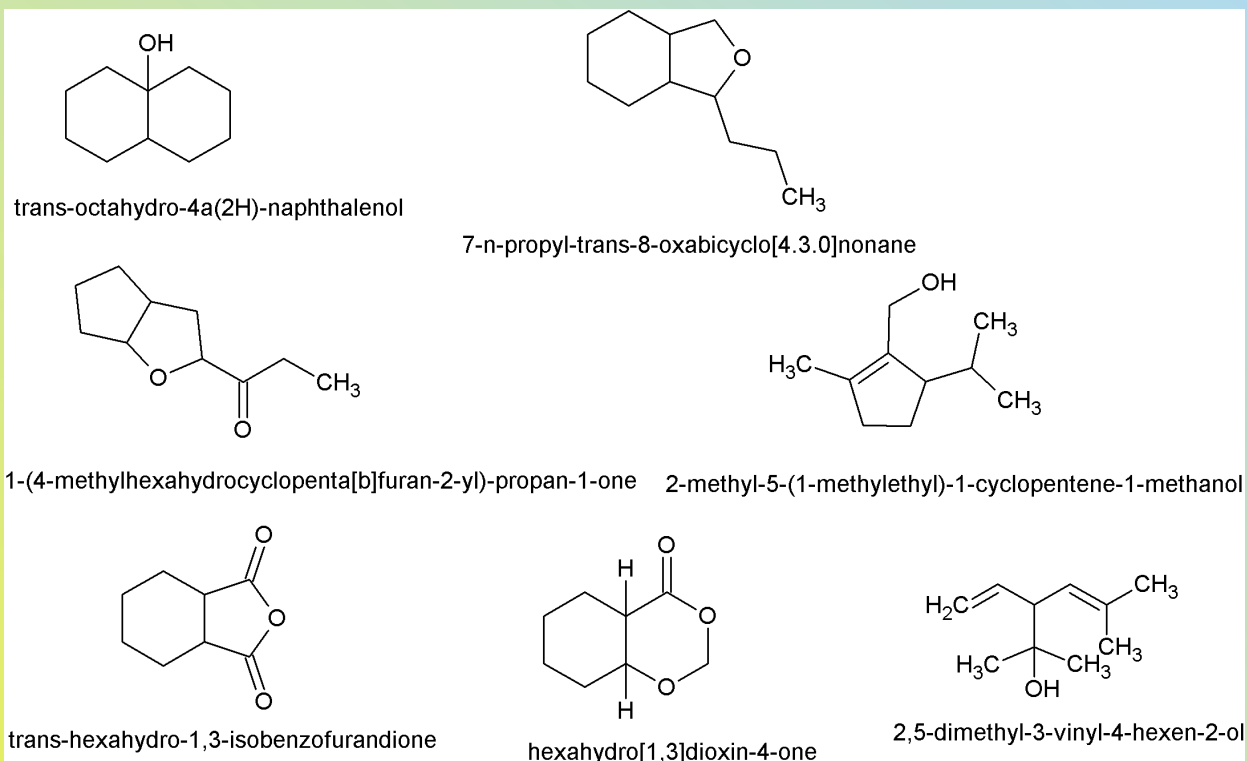
2-cyclohexen-1-one



- Cyclopentanones and cyclohexanones peaked around NTC start

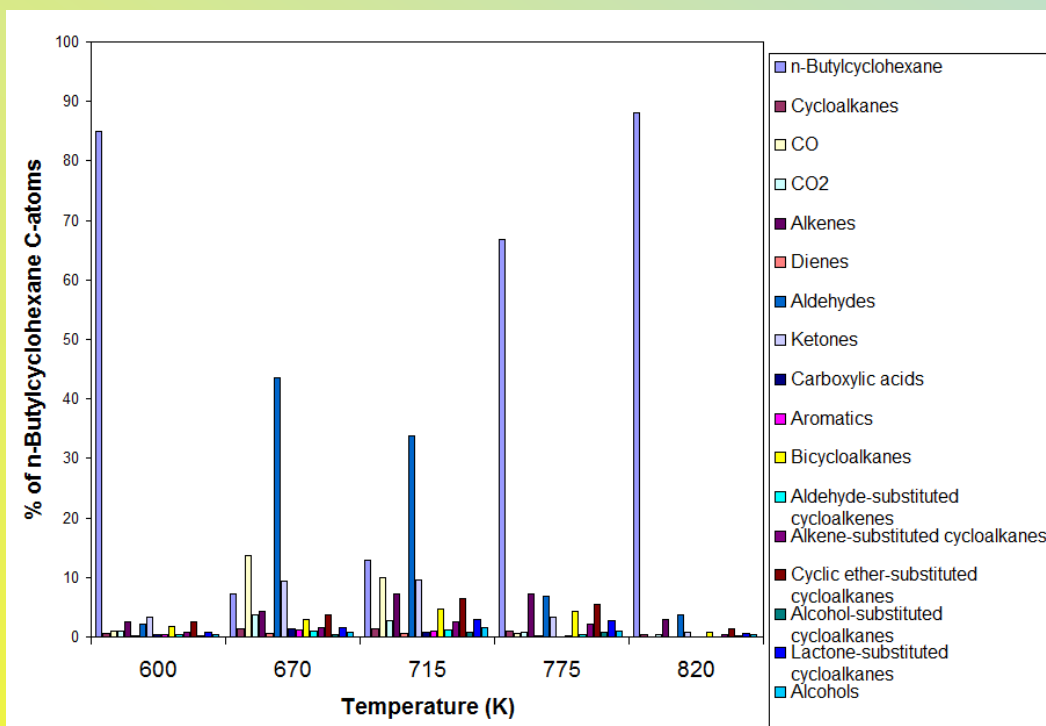
Other Select Species from n-BCH

- A dicyclohexane, tetrahydrofuran-substituted cyclohexanes, lactone-substituted cyclohexanes, an alkylated C₁₀ cyclopentene, and an alkylated C₁₀ diene were measured at relatively significant (>10 ppm) quantities, particularly in the NTC region



- In high temperature n-propylcyclohexane oxidation, Ristori et al. (2001) considered isomerization of cyclohexyl radicals to yield alkenyl radicals, similar to our observation of 2,5-dimethyl-3-vinyl-4-hexen-2-ol

Class Analysis - n-BCH



All classes accounting for $\geq 1\%$ of reactant, fractions of reactant and product calculated by C-atoms

Temperature (K)	600	670	715	775	820
Classes accounting for $\geq 5\%$ of reactant, listed in descending order	n-BCH	aldehydes, CO, ketones, n-BCH	aldehydes, n-BCH, CO, ketones, alkenes, cyclic ether-substituted cycloalkanes, bicycloalkanes	n-BCH, alkenes, aldehydes, cyclic ether-substituted cycloalkanes	n-BCH

Highlights of n-BCH Work

- **n-Butylcyclohexane experiments were conducted with carbon balances greater than 95% in the new setup, measuring 65 intermediates**
- **C₂₋₄ straight-chain alkenes produced from n-butyl chain**
- **Larger species measured were cycloalkenes, cycloketones, and multi-ring species (cycloalkane / tetrahydrofuran, cycloalkane / lactone, and dicycloalkane)**
- **Different classes were predominant at different reaction conditions:**
 - **low temperature (aldehydes, cycloketones, and acetic acid)**
 - **over the NTC region (cycloalkenes and multi-ring species)**

Summary and Future Work

- **The PFR facility has been modified to improve the carbon balance**
 - **Sample storage was eliminated**
 - **Stainless steel lines were replaced with glass-lined stainless steel**
 - **Controlled Cool Down now a Staged Cool Down**
- **n-Dodecane was studied at 550-830 K, 8 atm, $\phi = 0.2$**
- **n-Butylcyclohexane was studied at 600-820 K, 8 atm, $\phi = 0.4$**
- **Similar classes of intermediates were formed in both studies suggesting similar low temperature behavior**
- **Next hydrocarbon will be selected with the consortium**